

Electronic Supplementary Information

Room-Temperature Phosphorescence of Water-soluble Supramolecular Organic Framework

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Table of contents

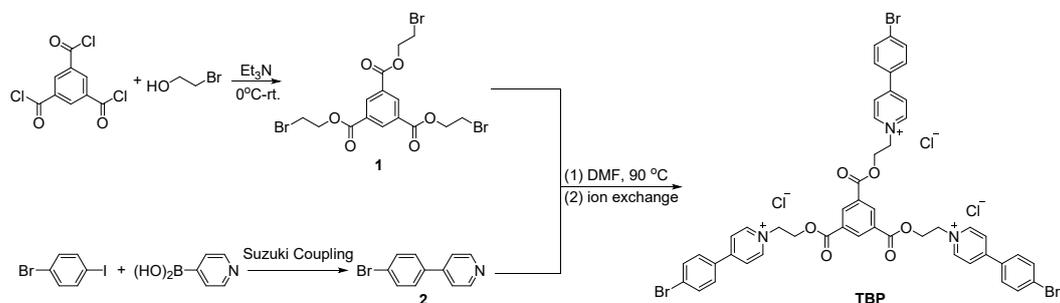
1. Materials and general procedures	S2
2. Synthesis and characterization of TBP	S2
3. Characterization of CB[8]-TBP complex.....	S6
4. Reference	S8

1. Materials and general procedures.

1.1 Materials. All reagents were purchased from Adamas-beta® or TCI Chemicals and used without further purification. Solvents were purified according to standard laboratory methods. The molecular structures were confirmed using ^1H NMR, ^{13}C NMR and high-resolution ESI mass spectroscopy.

1.2 General methods. All reagents used for the synthesis or measurements were commercially available without further purification. Water used in tests and to prepare solution was ultrapure. ^1H NMR and ^{13}C NMR spectra were recorded on Brüker AV-400 and Brüker AV-600 spectrometers. Coupling constants J are given in Hz. Chemical shifts were shown in ppm relative to the solvent residual peak was used as the internal standard. Molecular masses were determined by a Waters LCT premier XE spectrometer. The UV-Vis absorption spectra and PL spectra were performed on a Varian Cray 500 spectrophotometer and a Horiba Fluoromax-4 at 25 °C, respectively. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1} . Absolute PL quantum yield was determined with a spectrometer C11347-11 (Hamamatsu, Japan). Isothermal titration calorimetry (ITC) data was recorded on TA Instruments NANO ITC at 25°C in aqueous solution, the host compound (CB[8], 50 μM) was in the injection syringe, and guest compound (TBP, 3.3 μM) was in the sample cell. High-resolution Transmission Electron Microscopy (HRTEM) images were taken on JEOL JEM2100 electron microscope at an accelerating voltage of 200 kV. TEM samples were prepared by casting a small amount of sample on a perforated copper grid (200 mesh) covered with a carbon film and dried in air.

2. Synthesis and characterization of TBP.



Scheme S1 Synthetic route of TBP.

Synthesis of tris(2-bromoethyl) benzene-1,3,5-tricarboxylate (1). 3-Bromopropanol (500 mg, 4 mmol, 4.0 eq) was dissolved in 5 mL dry dichloromethane. Triethylamine (0.6 mL, 4 mmol, 4.0 eq) was added and the mixture was stirred at 0 °C for 30 mins. After dropwise addition of dry dichloromethane solution of 1,3,5-benzenetricarbonyl trichloride (1 mmol, 0.5 M), the resulting mixture was stirred at 0 °C for 2 h and warmed to room temperature stirring for another 16 h and then it was filtered. The filtrate was washed sequentially with saturated sodium hydrogen carbonate solution and saturated brine and dried over sodium sulfate. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica (petroleum ether/dichloromethane = 3:1) to give compound **1** (white solid, 465 mg, 88 % yield).

Synthesis of 4-(4-bromophenyl)-pyridine (2). Compound **2** was obtained from 1-bromo-4-iodobenzene and pyridine-4-boronic acid with Suzuki coupling reaction.^[1]

Synthesis of 1,1',1''-(((benzene-1,3,5-tricarbonyl)tris(oxy))tris(ethane-2,1-diyl))tris(4-(4-bromophenyl)pyridin-1-ium) trichloride (TBP).

Compound **1** (266 mg, 0.5 mmol, 1.0 eq) and **2** (583 mg, 2.5 mmol, 5.0 eq) were dissolved in DMF (6.0 mL), and the mixture was stirred at 90 °C for 4 days. After cooling the reaction mixture to room temperature, diethyl ether was added to give an orange solid precipitate. This solid was separated by filtration under reduced pressure and was dissolved in ultrapure water, and aqueous NH₄PF₆ was added dropwise until no further precipitation was observed. The precipitate was filtrated and washed with H₂O for several times. After air drying, it was redissolved in acetonitrile with subsequent addition of aqueous (n-Bu)₄NCl solution to yield the light yellow precipitate, which was collected and washed with acetonitrile to give crude product. The resulting crude product was recrystallized in water by slowly evaporating solvent to give pure **TBP** (white fibrous crystals, 100 mg, 18.3 % yield). ¹H NMR (DMSO-*d*₆, 400 MHz, TMS) δ 9.39 (d, *J* = 6.8 Hz, 6H), 8.55-8.59 (m, 9H), 8.02 (d, *J* = 8.8 Hz, 6H), 7.84 (d, *J* = 8.8 Hz, 6H), 5.17 (t, *J* = 4.8 Hz, 6H), 4.89 (t, *J* = 4.8 Hz, 6H). ¹³C NMR (DMSO-*d*₆, 100 MHz, TMS) δ 164.1, 154.5, 146.1, 134.5, 133.1, 133.0, 131.1, 130.6, 126.9, 124.8, 64.7, 58.8. HRMS (ESI) calcd. for C₄₈H₃₉N₃O₆Cl₂Br₃ (M-Cl)⁺: 1059.9766, Found: 1059.9790.

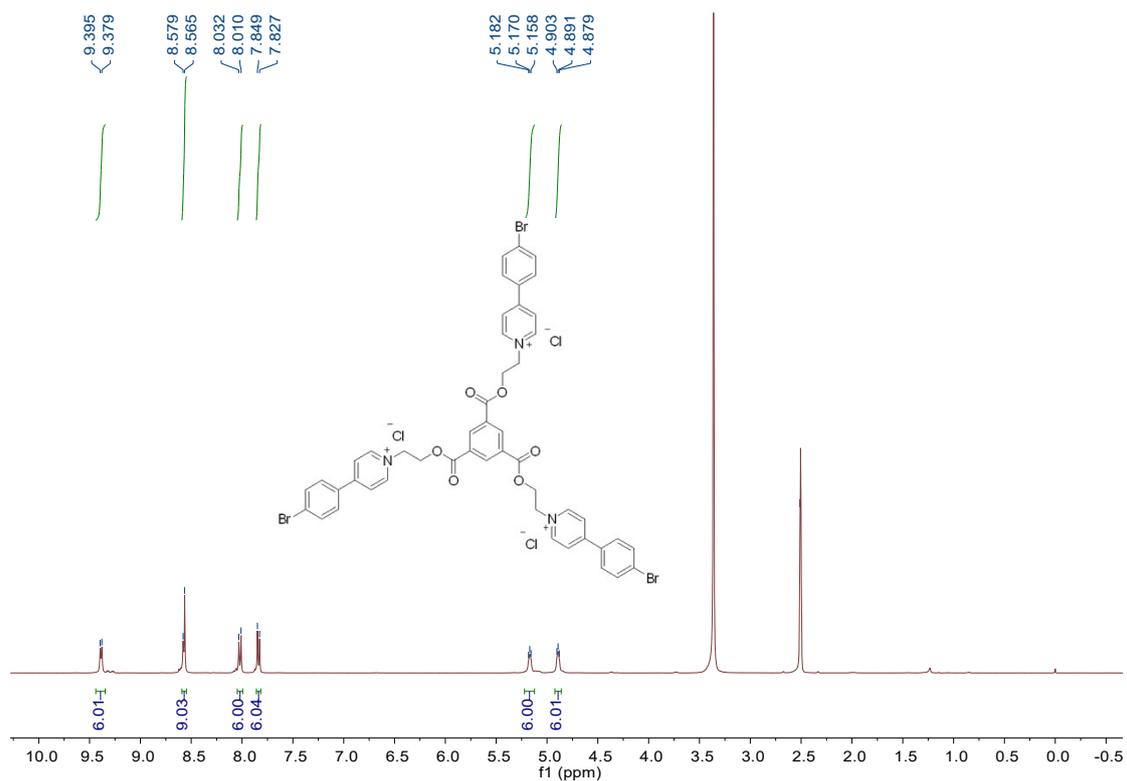


Fig. S1 ^1H NMR spectrum (400 MHz) of TBP in $\text{DMSO-}d_6$.

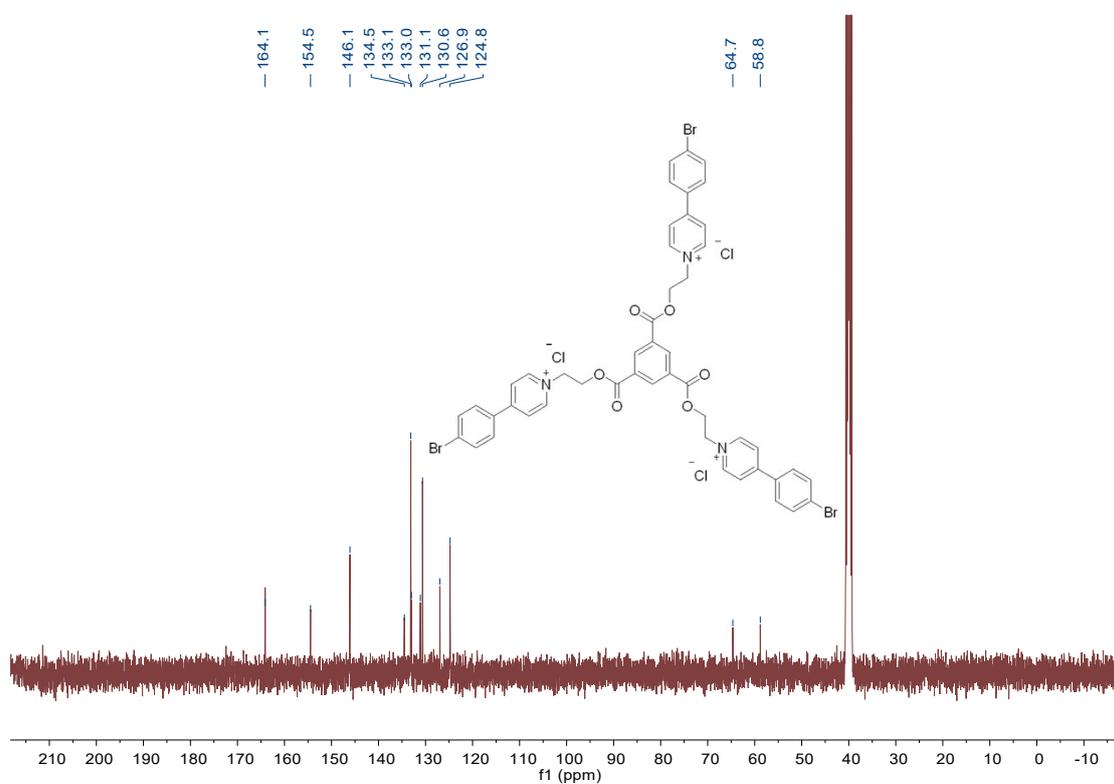


Fig. S2 ^{13}C NMR spectrum (100 MHz) of TBP in $\text{DMSO-}d_6$.

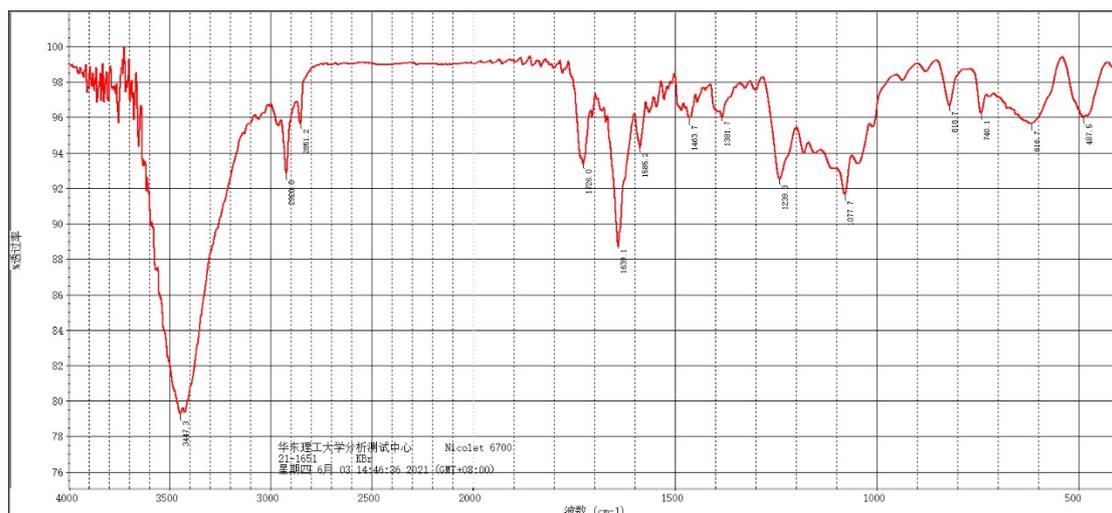


Fig. S3 FT-IR absorbance spectrum of **TBP**, 298 K.

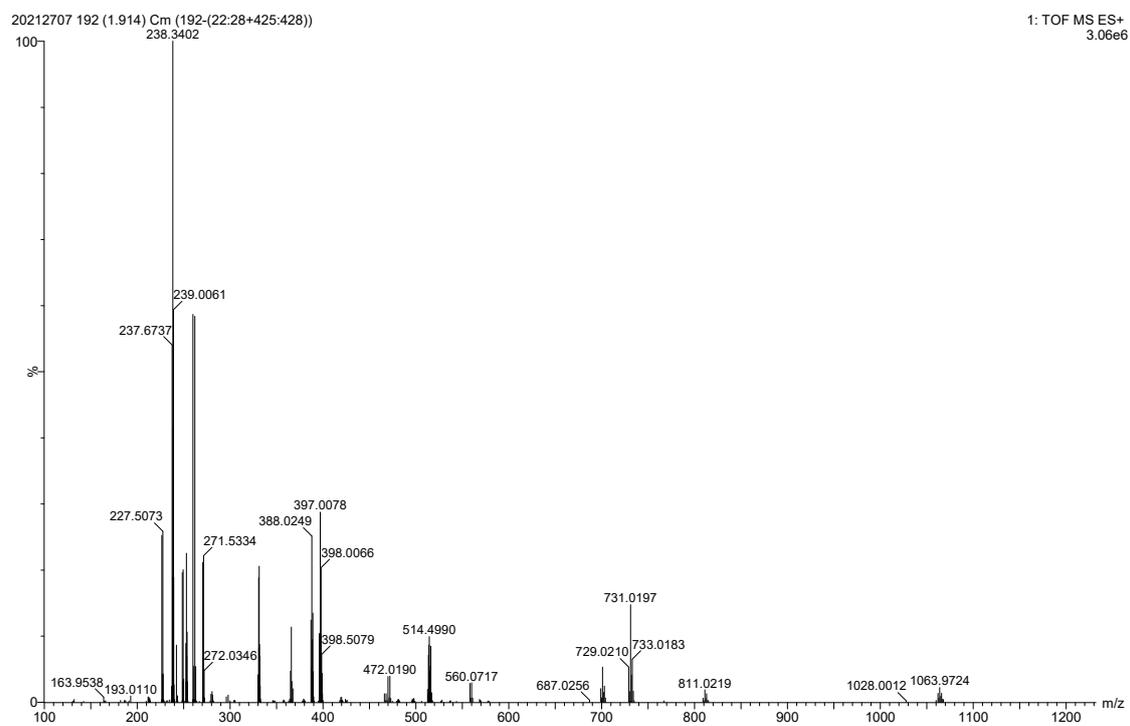


Fig. S4 HRESI-MS spectrum of **TBP**.

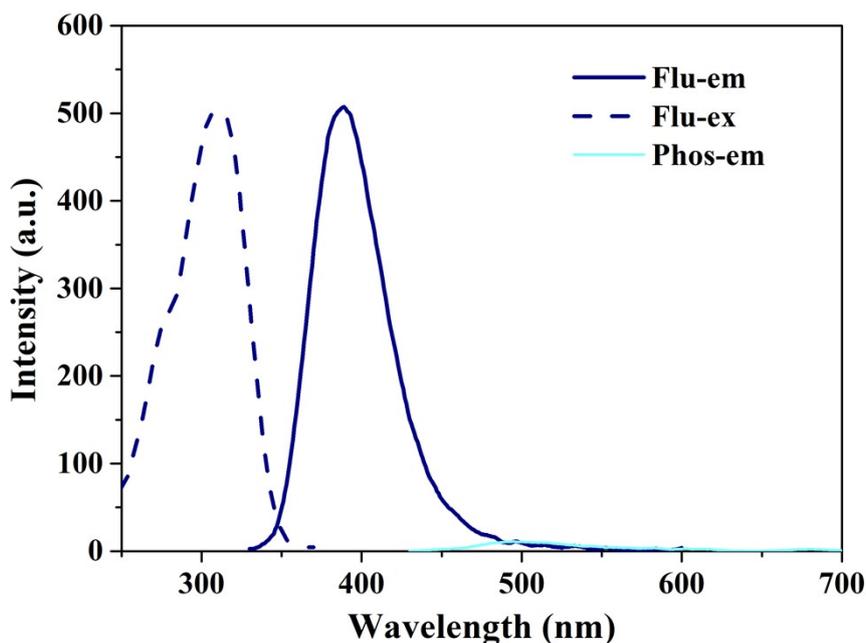


Fig. S5 Fluorescence excitation (deep blue dashed line) and emission (deep blue solid line) spectra of aqueous **TBP** solution (3.3×10^{-6} M, excitation slit = emission slit = 5 nm, PMT voltage = 700 V); phosphorescence spectrum (cyan solid line) of aqueous **TBP** solution (3.3×10^{-6} M, $\lambda_{\text{ex}} = 315$ nm, excitation slit = emission slit = 10 nm, PMT voltage = 800 V, delay time = 0.2 ms).

3. Characterization of CB[8]-TBP complex.

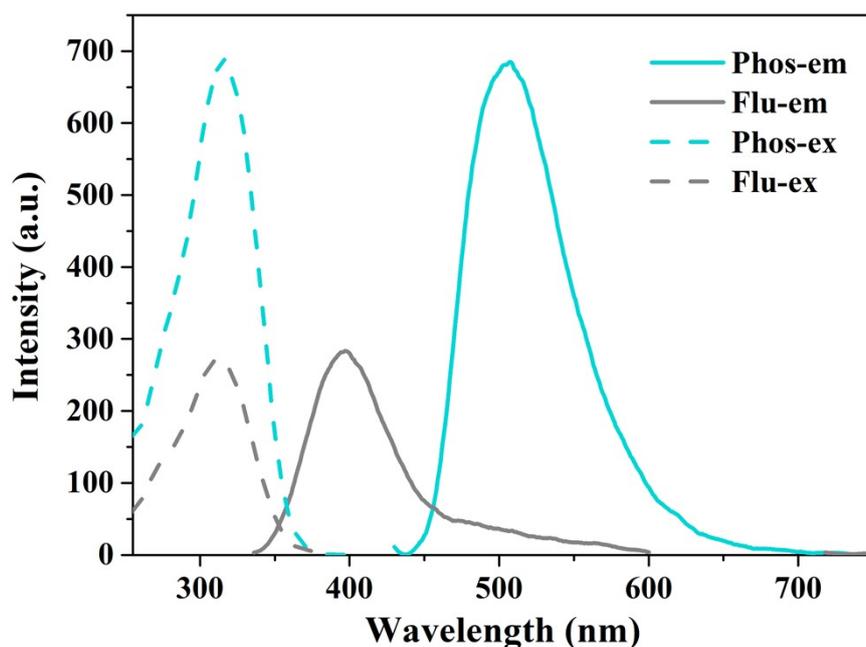
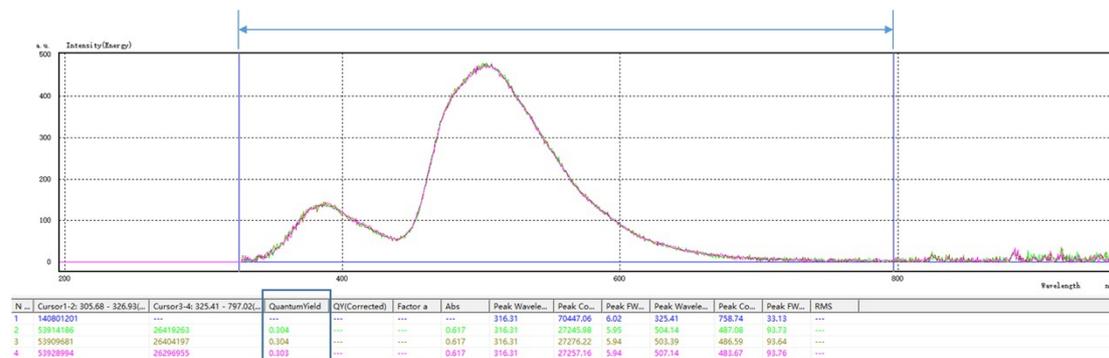


Fig. S6 Spectra of **CB[8]-TBP** assembly (3/2, v/v) in H_2O (**TBP**: 3.3×10^{-6} M, **CB[8]** 5×10^{-6} M):

fluorescence excitation (grey dashed line) and emission (grey solid line) spectra (excitation slit = emission slit = 5 nm, PMT voltage = 800 V); phosphorescence excitation (cyan dashed line) and emission (cyan solid line) spectra (excitation slit = emission slit = 10 nm, PMT voltage = 800 V, delay time = 0.2 ms).



QY = 30.4%

Fig. S7 The PL quantum yield of **film-SOF** at 298 K ($\lambda_{ex} = 315$ nm).

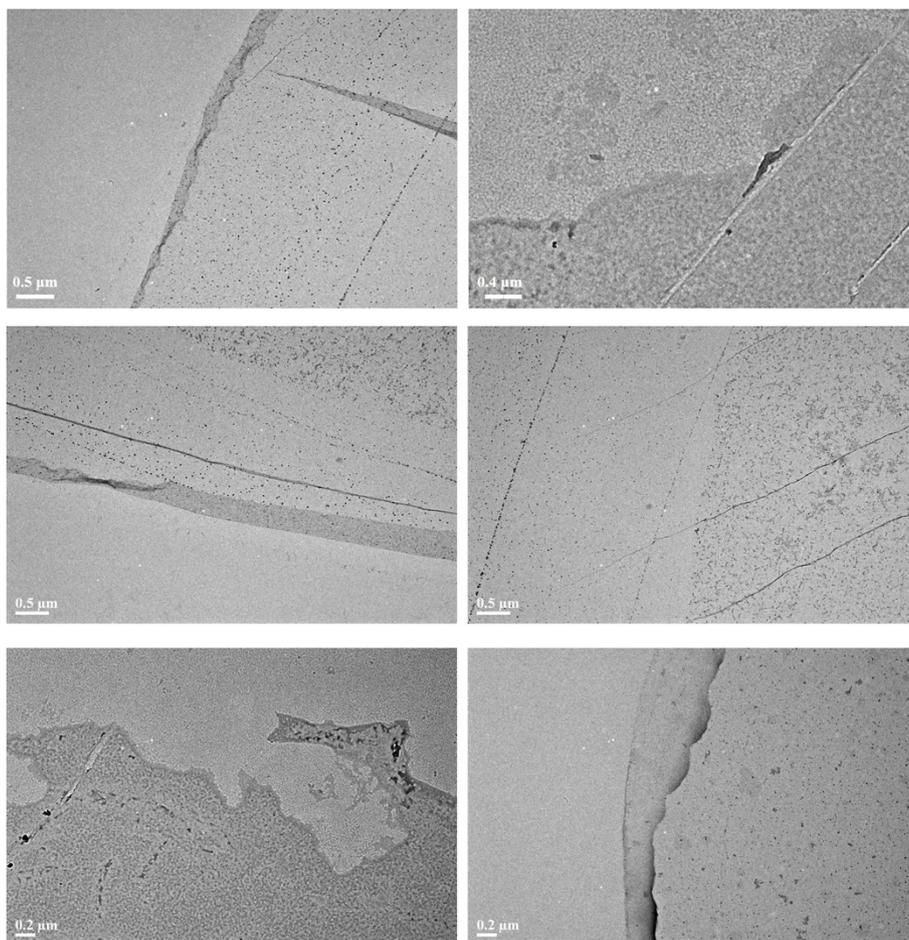


Fig. S8 TEM images of **CB[8]-TBP** assembly (3/2, v/v) in H_2O (TBP: 3.3×10^{-6} M, CB[8] 5×10^{-6} M) at 298 K.

4. Reference.

- [1] H. L. Ozores, M. Amorín, J. R. Granja, *J. Am. Chem. Soc.* **2017**, *139*, 776.